Contribution from the
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The Metal - Metal Interaction in Coordination Compounds. Magnetic Properties. I. The $d^n d^n$ Electron Systems with Negative Exchange Integral.

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The expressions for the magnetic susceptibility of the Me-Me (Metal-Metal) system of a d^n d^n electronic configuration are derived, where n = 1, 2, 3, 4, 5. Theoretical curves of magnetic susceptibility versus temperature have been plotted for these systems at different negative values of the exchange integral J. The relationship between the value of this integral and T_N (Néel temperature) as well as between the μ_{eff} and electronic structure of the Me-Me system has been studied.

Introduction

Te magnetic properties of coordination compounds exhibiting the Me-Me (Metal-Metal) interaction have been examined in numerous experimental and theoretical investigations.[1-38] The systems of this type exist most frequently in the case of transition metals binuclear complexes withe one, two- or three-bridges among the central ions. The maximum of magnetic susceptibility, depending on the temperature has been confirmed in these compounds, what proves their antiferromagnetic properties.

Earnshaw and Lewis[14] formulated the magnetic susceptibility taking into account the spin-spin interaction for a Me-Me system with spins (5/2, 5/2), (3/2, 3/2), (1/2, 1/2). Such calculations for the binuclear Cu^{2+} complexes were made erlier by Figgis and Martin.[3] It seemed purpeseful to derive equations for the Me-Me system wiht spins (1, 1) and (2, 2) and to examine the relationship between the magnetic susceptibility and temperature for all te five systems in order to establish the relation between the exchange integral J and Néel temperature T_N. The formulas for magnetic susceptibility of the spin system (5/2, 5/2), (3/2, 3/2), (1/2, 1/2) have also been derived.

Calculations

The spin-spin interaction energy for a two spins system is, according to Heisenberg, given by the equation:

$$E^{\circ}(S) = -JS_1S_2 \qquad (1)$$

where J is the exchange integral, and

$$S_1S_2 = 1/2[S(S+1) - S_1(S_1+1) - S_2(S_2+1)] \qquad (2)$$

S assumes the values of S_1+S_2, S_1+S_2-1, ..., $|S_1-S_2|$. These equations were used to calculate the energie levels for particular spins systems. The results are given in Table I.

The magnetic susceptibility was calculated by formula:

$$\chi = \frac{N\dfrac{g^2\beta^2}{kT}\sum\limits_{S}\sum\limits_{M_S=-S}^{S} M_S{}^2 \exp\left[-\dfrac{E^{\circ}(S)}{kT}\right]}{\sum\limits_{S}\sum\limits_{M_S=-S}^{S} \exp\left[-\dfrac{E^{\circ}(S)}{kT}\right]} \qquad (3)$$

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Table I. Magnetic susceptibility and energy levels of the Me-Me system with a $d^n d^n$ electronic configuration

Electronic structure	S_1	S_2	S	$-JS_1S_2$		$\chi = N\frac{g^2\beta^2}{kT}\sum\limits_{S}\sum\limits_{M_s=-S}^{S} M_s^2 \exp\left[-\frac{E^0(S)}{kT}\right] \Big/ \sum\limits_{S}\sum\limits_{M_s=-S}^{S} \exp\left[-\frac{E^0(S)}{kT}\right]$	No
				$-1/2\ J[S(S+1)]$	$1/2\ J[S_1(S_1+1)+S_2(S_2+1)]$		
d^1d^1	1/2	1/2	1 0	$-J$ 0	$+3/4\ J$ $+3/4\ J$	$\chi = N\frac{g^2\beta^2}{2kT}\frac{4}{3+\exp(-J/kT)}$	(1'
d^2d^2	1	1	2 1 0	$-3J$ $-J$ 0	$+2\ J$ $+2\ J$ $+2\ J$	$\chi = N\frac{g^2\beta^2}{kT}\frac{10+2\exp(-2J/kT)}{5+3\exp(-2J/kT)+\exp(-3J/kT)}$	(2'
d^3d^3	3/2	3/2	3 2 1 0	$-6J$ $-3J$ $-J$ 0	$+15/4\ J$ $+15/4\ J$ $+15/4\ J$ $+15/4\ J$	$\chi = N\frac{g^2\beta^2}{kT}\frac{2\exp(-5J/kT)+10\exp(-3J/kT)+28}{7+5\exp(-3J/kT)+3\exp(-5J/kT)+\exp(-6J/kT)}$	(3'
d^4d^4	2	2	4 3 2 1 0	$-10J$ $-6J$ $-3J$ $-J$ 0	$+6\ J$ $+6\ J$ $+6\ J$ $+6\ J$ $+6\ J$	$\chi = N\frac{g^2\beta^2}{kT}\frac{60+28\exp(-4J/kT)+10\exp(-7J/kT)+2\exp(-9J/kT)}{9+7\exp(-4J/kT)+5\exp(-7J/kT)+3\exp(-9J/kT)+\exp(-10J/kT)}$	(4')
d^5d^5	5/2	5/2	5 4 3 2 1 0	$-15J$ $-10J$ $-6J$ $-3J$ $-J$ 0	$+35/4\ J$ $+35/4\ J$ $+35/4\ J$ $+35/4\ J$ $+35/4\ J$ $+35/4\ J$	$\chi = N\frac{g^2\beta^2}{kT}\frac{110+60\exp(-5J/kT)+28\exp(-7J/kT)+10\exp(-12J/kT)+2\exp(-14J/kT)}{11+9\exp(-5J/kT)+7\exp(-9J/kT)+5\exp(-12J/kT)+3\exp(-14J/kT)+\exp(-15J/kT)}$	(5')

where g is the spectroscopic splitting factor, β is the Bohr's magneton, k is Boltzmann's constant, T is the temperature. This formula results from the Van Vleck's formula[39] if the Zeeman effect for the Me-Me system will be taken into account. The results are presented in Table I.

The numerical values of magnetic susceptibility for particular spin systems have also been calculated. The calculations were carried out for J assuming the values of 0, —10, —20, —30, —40, —50, —100, —150 ..... —500 cm^{-1} and T lying in the range: 10, 20, 30, ... 300°K for each value of J. The results were computed in the Department of Numerical Methods of the Wroclaw University in an ELLIOTT-803 computer. Some more interesting results of these calculations are shown in Figures 1-5, where J is given in cm^{-1}, and the magnetic moments (in Bohr magneton μ_B) are related to one metal ion with a d^n electron structure, and Θ is a constant in the Curie-Weiss equation :

$$\chi = C/(T-\Theta) \tag{4}$$

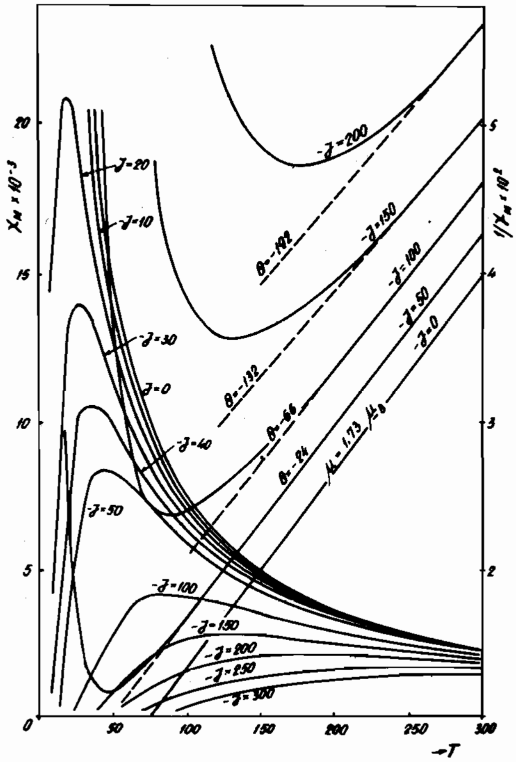

Figure 1. Magnetic susceptibility curves and their reciprocals for various J values according to the temperature for a d^1 d^1 electronic structure of the Me-Me system.

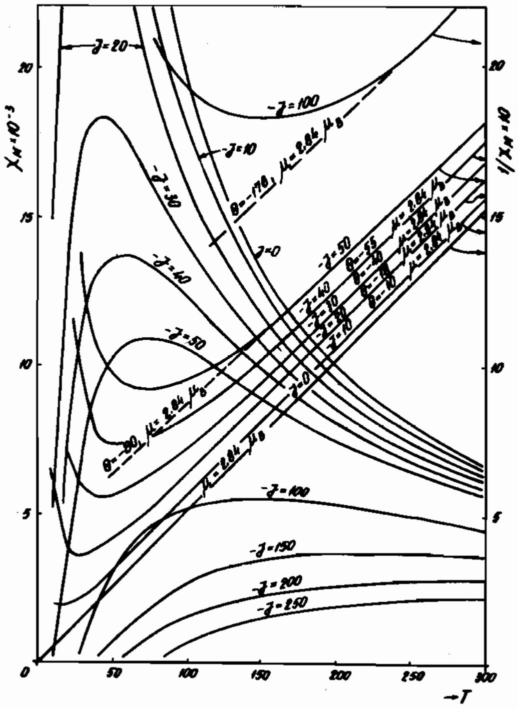

Figure 2. Magnetic susceptibility curves and their reciprocals for various J values according to the temperature for a d^2 d^2 electronic structure of the Me-Me system.

Results and Discussion

The calculated curves giving the plot of magnetic susceptibility versus temperature enable to draw out the following conclusions:

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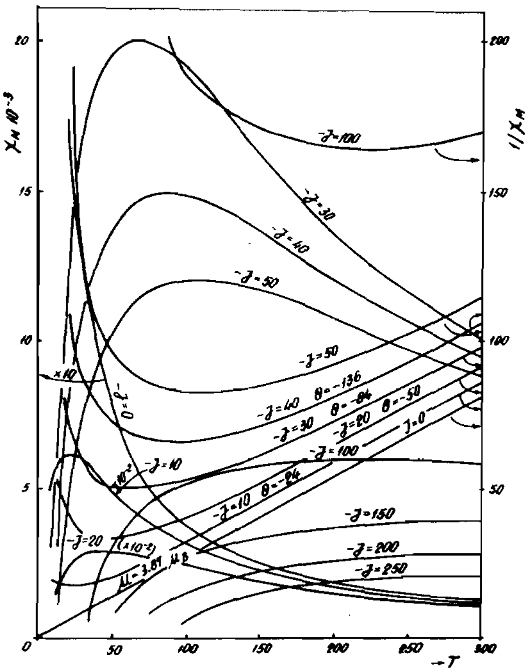

Figure 3. Magnetic susceptibility curves and their reciprocals for various J values according to the temperature for a $d^3 d^3$ electronic structure of the Me-Me system.

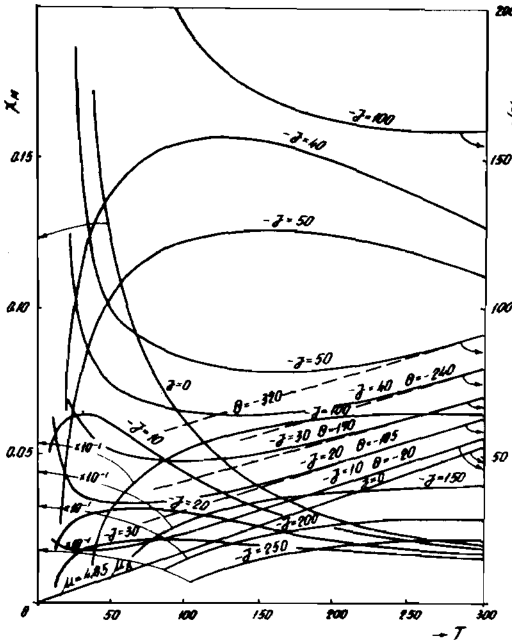

Figure 4. Magnetic susceptibility curves and their reciprocals for various J values according to the temperature for a $d^4 d^4$ electronic structure of the Me-Me system.

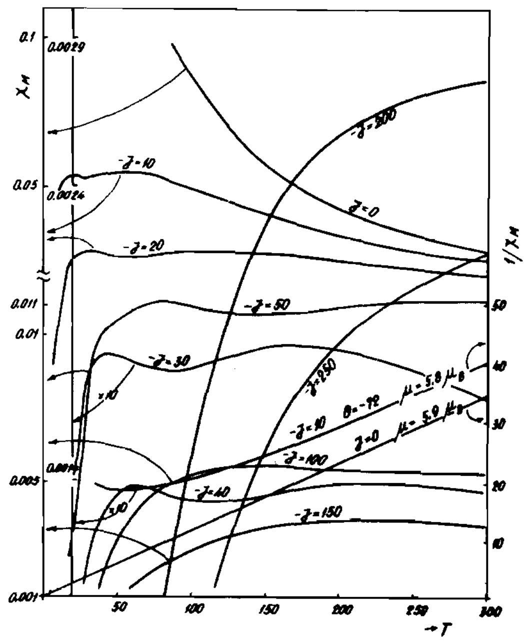

Figure 5. Magnetic susceptibility curves and their reciprocals for various J values according to the temperature for a $d^5 d^5$ electronic structure of the Me-Me system.

(1) The magnetic susceptibility decreases as the values of (—J) increase.

(2) The Curie-Weiss law is obeyed over the paramagnetic range and the calculated magnetic moment per one metal atom is equal to the theoretical value calculated from equation:

$$\mu = \sqrt{n(n+2)}\mu_B. \tag{5}$$

The magnetic moment calculated for equation

$$\mu_{eff} = 2.84\ \sqrt{\chi_M T}\ \mu_B \tag{6}$$

decreases with the temperature. The changes of these magnetic moments according to the temperature for one metal atom in the system Me-Me are presented in Figures 6-10.

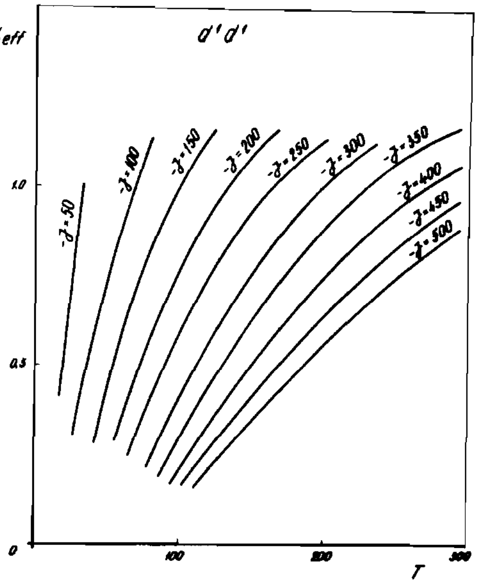

Figure 6. Dependence of the magnetic moment on the temperature and value of the exchange integral J for a $d^1 d^1$ electronic structure of the Me-Me system.

It is interesting to note that for the (—J) values (in cm^{-1}) equal to or higher than the T values the magnetic moment calculated from the Curie law is approximately constant for all the discussed electronic configurations in a system Me-Me.

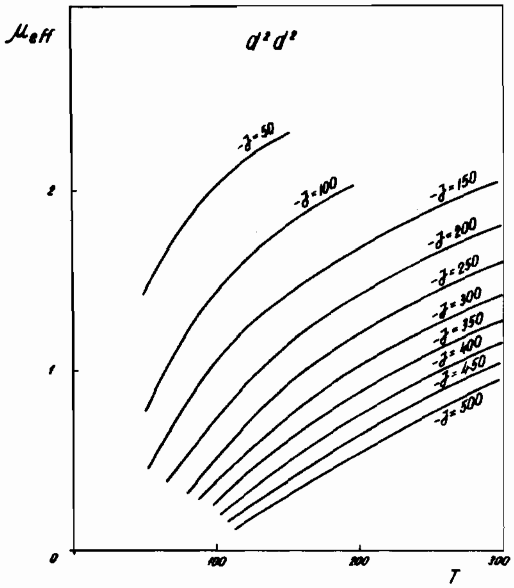

Figure 7. Dependence of the magnetic moment on the temperature and value of the exchange integral J for a d^2d^2 electronic structure of the Me-Me system.

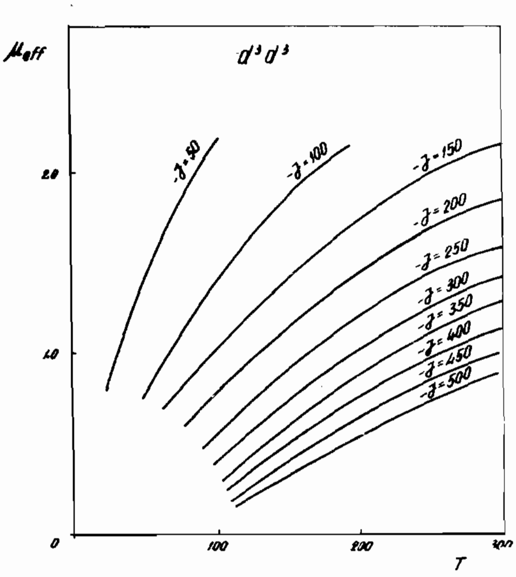

Figure 8. Dependence of the magnetic moment on the temperature and value of the exchange integral J for a d^3d^3 electronic structure of the Me-Me system.

(3) For a given electronic structure of the system Me-Me the Néel temperature depends linearly on the value of the exchange integral (—J).

An interesting relation between the magnetic susceptibility and temperature is shown by the curves calculated for the (5/2, 5/2) electrons spins. These curves possess two maxima each (Figures 5 and 10, and Table II) which corresponds to the two Néel temperatures.

No effect of the orbital moment on the magnetic susceptibilities was taken into account in the above calculations which is a certain approximation. This influence may be neglected in case of the compounds of d-electron elements. For this reason the results

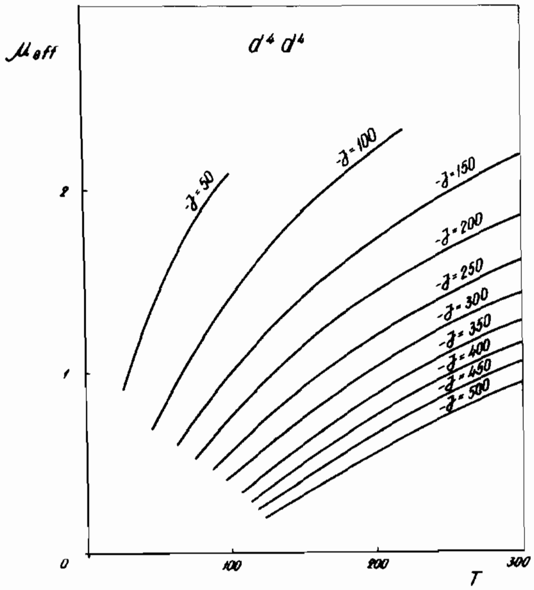

Figure 9. Dependence of the magnetic moment on the temperature and value of the exchange integral J for a d^4d^4 electronic structure of the Me-Me system.

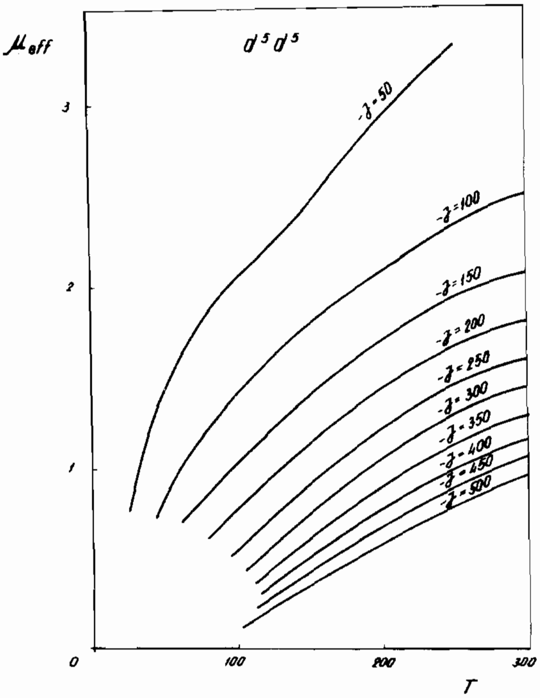

Figure 10. Dependence of the magnetic moment on the temperature and value of the exchange integral J for a d^5d^5 electronic structure of the Me-Me system.

Table II. Dependence between the T_{N_1} and T_{N_2} temperatures and exchange integral J for a d^5d^5 electronic structure of the Me-Me system

—J (in cm^{-1})	T_{N_1}	T_{N_2}
10	15	60
20	30	115
30	45	170
40	62	225
50	80	285

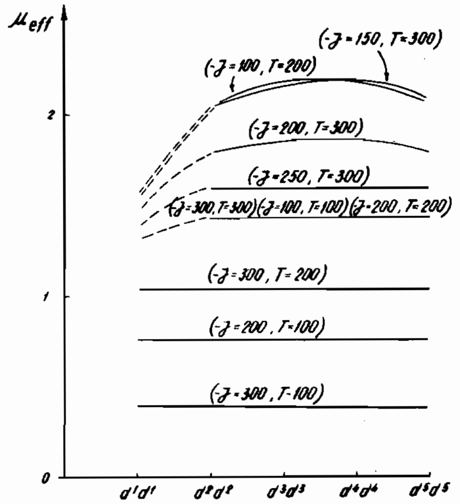

Figure 11. A plot of the magnetic moment versus the electronic structure of the Me-Me system at constant T and (—J) values.

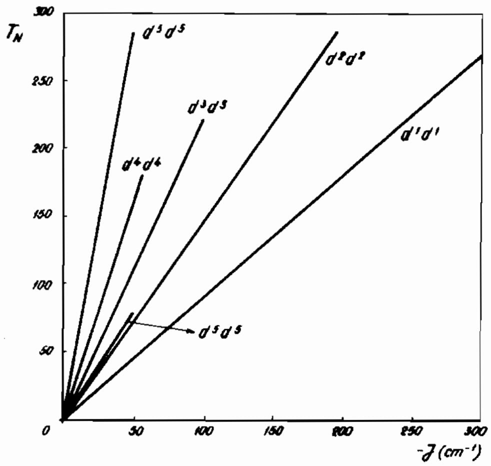

Figure 12. Relationship between the Néel temperature and exchange integral J for a $d^n d^n$ electronic structure of the Me-Me system.

obtained are valid for the majority of these compounds. These results are also valid for a $d^n d^n$ electronic structure in the Me-Me system where $10 > n > 5$ since

$$\chi\,(d^n\,d^n) = \chi\,(d^{10-n}\,d^{10-n}) \qquad (7)$$

In case of the complex compounds, the crystal field may change the number of unpaired d electrons of the central ions in comparison to a free metal ion. In this case the magnetic susceptibility of the Me-Me system is described by the equation (7), where n is the number of unpaired electrons of the metal ion.

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